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### THE EFFECT OF PRESSURE ON THE MASS TRANSFER BETWEEN MAGMATIC MELT AND WATER OF THE EXTERNAL MEDIUM

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An estimate is given on the influence of water pressure in magma pores, hydrostatic pressure exerted on the melts, and water content in the melt itself on the mass transfer between magmatic melts and water of the external medium. A simple binary system of a volatile component and a silicate melt in equilibrium is used as physical model in deriving equations for calculating the equilibrium of the albite - water system, taking the osmotic effect and the influence of gravitation into consideration. An increase in water vapor pressure increases the equilibrium concentration of water while an increase in the pressure of the overlying liquid column decreases this equilibrium. Apparently, the magma absorbs water in its lower layers and gives off water near the roof of the magma chamber, promoted by convection in the melt and diffu-Luthor sion toward the top.

The ability of magmatic melts to interact with the water of the external medium is one of the most complex problems of petrology. In many geological conceptions, based on the view that the surrounding matter exerts a great influence on the magmatic processes and especially on the processes of ore forma-

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tion, mass transfer between the magmatic melts and the water of the enclosing rocks is assumed to be very active. Other workers believe that this mass transfer, at least at great depths, is limited because of the extremely slight permeability of crystalline rocks at high pressure. Both views find confirmation in geological facts. Obviously both these cases are entirely possible, depending on the particular circumstances.

Since water is a highly volatile component, the direction of mass transfer between the extraneous water and the magma can to some extent be estimated in terms of the pressure of the water in the enclosing rocks and the pressures exerted on the melts. With this object, we considered a simple binary system consisting of a volatile component and a silicate melt in equilibrium, under conditions selected on the basis of certain geological facts and assumptions as to the character of these pressures.

This approach is to some extent an abstraction of the natural processes, but apparently is unavoidable at the present state of knowledge on the physicochemical properties of magmas. In this connection, the thermodynamic calculations performed in this work have only one object: to evaluate, in terms of the pressures, the most general trend of the influence exerted by the tendency of magmas toward chemical equilibrium with the water of the enclosing rocks.

As a result we sought the answers to the following questions: How is the process of absorption and loss of water by magmas correlated with the vapor pressure of the water in the enclosing rocks, with the pressure in the column of melt, and with the initial concentration of water in the magma? What influence might be exerted on this mass transfer by the tendency of the magmas toward a definite distribution of water over the height of the magmatic chamber, under the influence of the gravitational and temperature fields? What is the principal

tendency of the variation in mass transfer for water, with varying depth of deposition of the magmatic chamber?

#### 1. Physicochemical Model of the Process

Starting from the experimental data and geological observations, two fundamentally different cases can be distinguished for the water conditions in hard crystalline rocks. The first is connected with the open system of pores characteristic of shallow depths. The pressure of water in these pores must be \( \frac{508}{008} \) determined by the height of the column of vapor or liquid. Moreover, in such pores the water may move under a certain head, due to the most varied causes (Bibl.1 - 3).

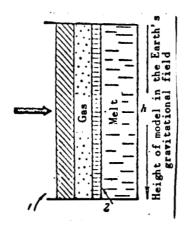


Fig.l Physical Model Adopted for Description of the Equilibrium of Water in the Enclosing Rock with the Magmatic Melts

1 - Piston creating a pressure on the gas; 2 - Partition permeable for gas and impermeable for the melt

The second case relates to the closed system of pores, which probably is located at great depth. In closed pores, the pressure of the water will be determined by its quantity in the pore interstices, by the temperature and by the strength of the pore walls. This pressure may reach considerable values, far

exceeding the lithostatic pressure of the enclosing rock (Bibl.2). If the pores are partially permeable, or if they are opened, the water may be expelled at high pressure, forming a jet of gas of a definite pressure (Bibl.2).

Thus in all cases under study, water in the liquid or vapor state must be considered as an independent medium capable of exerting pressure on the volume of the melt on contact with it.

The high viscosity of magmatic melts permits the assumption (confirmed by geological observations) that their penetration into the pores and intercrystal-line space of the enclosing rock must be extremely difficult, so that the hydrostatic pressure exerted by the magmatic fluid can be transmitted to the aqueous phase only partly or even not at all. This effect, first noted by Goranson (Bibl.6) and considered an osmotic effect by him, should be due to the inequality of pressure on the water in the enclosing rock and the melt.

Based on the above propositions, the physical model shown in Fig.1 is useful for describing the equilibria in the binary system formed by the volatile component and the melt, corresponding in first approximation to the conditions of equilibrium between the magmatic melts and the water of the enclosing rock. The model consists of a piston exerting pressure on the melt through a wall permeable to water and impermeable to the melt (Fig.1). The pressure of the piston is equivalent to the pressure of the water on the magma from the direction of the enclosing rock. The semipermeable wall reproduces the conditions of mechanical equilibrium under which the pressure exerted by the gas can be transmitted to the melt while the pressure exerted by the magmatic liquid cannot be transmitted to the gas.

At the model dimensions which are negligibly small with respect to the earth's gravitational field, the pressure on the melt will be equal only to the

gas pressure. All available experimental data on the equilibrium of water with silicate melts, by virtue of the experimental conditions (small mass of matter), are characterized by precisely such equilibria. Let us call this case "Model I".

If the model has a considerable extension in the gravitational field, i.e., for large masses of melt (let us call this case "Model II"), the pressure on the melt at each point over its height must be determined not only by the gas pressure but also by the pressure exerted by the weight of the overlying liquid column, i.e.,

$$P_{\text{melit}} = P_{\text{Hio}} + \int_{h=0}^{h} g \rho dh = P_{\text{Hio}} + P_{h}, \tag{1}$$

where  $P_{melt}$  is the pressure on the melt;  $P_{melt}$  is the pressure of the water /509 vapor due to the piston; h is the height of the column of melt;  $\rho$  is the density of the melt; g is the acceleration of gravity;  $P_h = \int_{h=0}^{h} g\rho dh$  is the pressure exerted by the weight of the overlying liquid column. The effect of gravitation on the pressure in the gas phase was neglected in first approximation.

From eq.(1) follows the necessary condition of equilibrium of the Model II, which, as noted above, must be observed in magmatic systems, namely,

$$P_{\text{melt}} + P_{\text{H,O}}$$

On transition to systems of considerable extension in the gravitational field (i.e., to Model II), the melt can no longer be regarded as a single phase, since the state of a large mass of matter in the presence of gravitation cannot be uniform. It will depend on the position of its particles in the earth's gravitational field. For this reason, in thermodynamics such systems are regarded as consisting of a continuous sequence of phases, each differing infinitely little from the adjacent phases (Bibl.4). This proposition defines the fundamental difference between Model I and Model II, i.e., the model which, from the thermodynamic viewpoint, can be the only true model for the description of

equilibrium in such large masses of magmatic melts as are found in nature.

Taking account of the influence of gravitation on the chemical equilibrium in the melt, the equilibrium of Model II can be described by the following differential equation:

$$RT d \ln f_{\text{H}_{\bullet}\text{O}} = \left(\frac{\partial \mu_{\text{H},\text{O}}}{\partial P_{\text{H}_{\bullet}\text{O}}}\right)_{T, h, N_{\text{H}_{\bullet}\text{O}}} dP_{\text{H}_{\bullet}\text{O}} + \left(\frac{\partial \mu_{\text{H},\text{O}}}{\partial h}\right)_{T, P_{\text{H}_{\bullet}\text{O}}} dh + \left(\frac{\partial \mu_{\text{H},\text{O}}}{\partial N_{\text{H}_{\bullet}\text{O}}}\right)_{T, h, P_{\text{H}_{\bullet}\text{O}}} dN_{\text{H}_{\bullet}\text{O}},$$

$$(2)$$

where  $f_{\text{H}_20}$  is the volatility of the extraneous water,  $\mu_{\text{H}_20}$  is the chemical potential of the water in the melt, and  $N_{\text{H}_20}$  is the molar fraction of water in the melt. Since

$$\left(\frac{\partial \mu_{\text{H}_{1}\text{O}}}{\partial P_{\text{H}_{2}\text{O}}}\right)_{T,h,N_{\text{H}_{2}\text{O}}} = \overline{V}_{\text{H}_{2}\text{O}}, \left(\frac{\partial \mu_{\text{H}_{2}\text{O}}}{\partial h}\right)_{T,P_{\text{H}_{2}\text{O}},N_{\text{H}_{2}\text{O}}} = \left(\overline{V}_{\text{H}_{2}\text{O}}\rho - M_{\text{H}_{2}\text{O}}\right) [5], dh = \frac{1}{g\rho} dP_{h}$$

and since [eq.(1)] the solubility of the water can be expressed in terms of its activity, it follows that, after suitable transformations of eq.(2), we obtain

$$RTd \ln f_{H_{s}O} = \overline{V}_{H_{s}O} dP_{H_{s}O} + \left(\overline{V}_{H_{s}O} - \frac{M_{H_{s}O}}{\rho}\right) dP_{h} + RTd \ln a_{H_{s}O}, \tag{3}$$

where  $\overline{V}_{H_{2}0}$  is the partial molar volume of water in the melt,  $M_{H_{2}0}$  is the molecular weight of the water,  $\rho$  is the density of the melt, and  $a_{H_{2}0}$  is the activity of the water in the melt.

A thermodynamic analysis of the equilibria between water and a silicate melt under the conditions of the osmotic effect (one of the necessary conditions of Model II) was first performed by Goranson (Bibl.6). Later, other investigators also became interested in similar equilibria in the magma (Bibl.7 - 10). These workers considered them on the basis of Goranson's concepts. The calculations of the osmotic effects were of great petrological interest, since they <u>/510</u> permitted a judgement as to how the environment might affect the water content

of magmas.

The formulation of the problem in this paper differs from Goranson's approach in that, in considering the models describing the equilibrium of the water of the enclosing rock with the magmatic melts, we took account not only of the osmotic effect but also of the influence of gravitation. As we have shown above, the latter is a necessary thermodynamic condition of equilibrium in large masses of magmatic melts.

#### 2. Calculations for the Albite - Water System

Using eq.(3) and the thermodynamic data obtained for the water - albite system (Bibl.11), let us define the variation in water content in an albitic melt with  $P_h$  height for the model II, at constant values of  $P_{H_{20}}$ .

This equilibrium can be described by the following differential equation:

$$RTd \ln N_{\rm H_sO} = -\left(\bar{V}_{\rm H_sO} - \frac{M_{\rm H_sO}}{\rho}\right) dP_h - RTd \ln \gamma_{\rm H_sO}. \tag{4}$$

After integration from  $P_h$  = 0 to the assigned values of  $P_h$  we obtain

$$\ln N_{\rm H_{2}O} = \ln N_{\rm H_{2}O}^{0} - \frac{1}{RT} \int_{P_{h=0}}^{P_{h}} \left( \overline{V}_{\rm H_{2}O} - \frac{M_{\rm H_{2}O}}{\rho} \right) dP_{h} - RT \ln \frac{\Upsilon_{\rm H_{2}O}}{\gamma_{\rm H_{2}O}^{0}}, \tag{5}$$

where  $N_{H_{20}}^{\circ}$  is the concentration of water in the melt at  $P_h$  = 0, and  $N_{H_{20}}$  is the concentration of the water in the melt at the assigned values of  $P_h$ ;  $\gamma_{H_{20}}^{\circ}$  and  $\gamma_{H_{20}}$  are the activity coefficients of the water dissolved in the melt at  $P_h$  = 0 and the assigned value of  $P_h$ , respectively.

In first approximation, let us assume that the partial molar volume of water  $\overline{V}_{H_20}$  is constant and equal to its value under the conditions of the initial integration point; let us neglect the dependence of the activity coefficients

of the water on  $P_n$ . We will also consider the density  $\rho$  of the water - albite melt as constant and equal to  $\sim 2~gm/cm^3$  (Bibl.11).

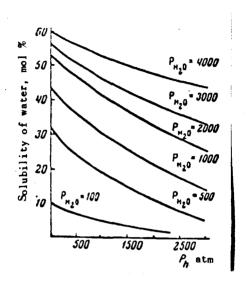


Fig.2 Solubility of Water in Albite Melts under Model II Conditions. Temperature 1200°C

Under these conditions eq.(5) is simplified to the following form:

$$\ln N_{\rm H_{2}O} = \ln N_{\rm H_{2}O}^{0} - \frac{\left(\overline{V}_{\rm H_{2}O} - \frac{M_{\rm H_{2}O}}{\rho}\right) \cdot P_{h}}{RT}$$
 (6)

Figures 2 and 3 show the results of calculations by this equation, in the form of several variants.

From these calculations, the concentration of water in albite solution is characterized by the following dependence on  $R_{H_20}$  and  $P_h$ : at  $P_h$  = constant, an increase in the water vapor pressure leads to an increase in the equilibrium concentration of water, while an increase of  $P_h$  at  $P_{H_20}$  = const decreases that equilibrium concentration of water (Fig.2).

In solving the problem of the osmotic equilibrium of water with the albite melt, neglecting the gravitational effect, similar relations were obtained (Bibl.6 - 9). With respect to the hydrostatic pressure, however, this agreement

is fortuitous as is obvious from the fact that, in eq.(4),  $\overline{V}_{H_{20}} > \frac{M_{H_{20}}}{\rho}$ . As a result, with increasing  $P_h$ , the concentration of water decreases. However, /511 for compounds or for T - P regions where  $\overline{V}_{H_{20}} < \frac{M_{H_{20}}}{\rho}$ , such a coincidence of tendencies cannot exist, and allowance for the gravitational nature of the hydrostatic pressure leads to fundamentally opposite relations.

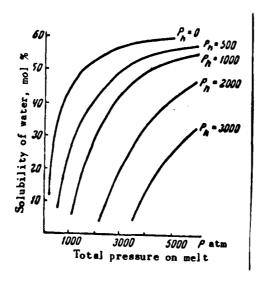


Fig.3 Solubility of Water in Albite Melt vs Total
Pressure on the Melt.

Heavy curve = content of water in a saturated
water - albite melt and Model I conditions; thin
curves = content of water under the equilibrium
conditions of Model II. Temperature 1200°C

### DISCUSSION

# 1. Influence of PH20, Ph, NH20 on Mass Transfer with Extraneous Water

Figure 3 shows the concentration of water in a water - albite melt as a function of the total pressure on the melt. The heavy lines show the limiting content of water in a saturated water - albite melt, according to Model I.

Above this curve is the two-phase region (water vapor and saturated water - albite melt) and below it is the single-phase region of the melt unsaturated

with water. The thin lines show the water content of the albite melt according to Model II, at constant values of  $P_h$ . All of the thin lines are located in the single-phase region of the system, i.e., in the region of the melt unsaturated with water.

From this it can be concluded that, in presence of mass transfer, magmatic melts saturated with water constitute an unstable system and should give off water.

This, of course, does not exclude the possible appearance of saturated magmas in nature but, in any case, does limit their existence in time.

In evaluating the ability of a magma to dissolve water, we usually start from the proposition that an unsaturated magma always absorbs water. In other

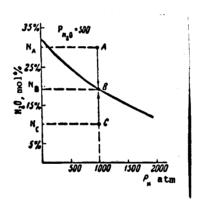


Fig.4 Example of Determining the Direction of a Diffusional Water Stream in the Magma, Based on Equilibrium of the Model II

Mass-transfer conditions:  $R_{\text{H}_{20}}$  = 500 atm,  $P_{\text{h}}$  = 1500 atm, point B - equilibrium concentration of water in melt. Magma with a water concentration of  $N_{\text{A}}$  >  $N_{\text{B}}$  will give off water, while magma with a water concentration of  $N_{\text{C}}$  <  $N_{\text{B}}$  will absorb it

words, the discussion is based on the Model I. However, on transition to the Model II, this is by no means the case.

As is generally known, the rate of diffusion processes in silicate melts is low. For this reason, for the large masses of melts met in nature, even

taking account of the geological time scales of their existence, the attainment of the equilibrium of Model II appears unlikely. If this is so, then mass /512 exchange should lead to the existence of diffusion flows of matter in the magma. The direction of such flows can be determined if the equilibrium state of the system, under the given conditions, is taken as a limit which this system is to approach, in exchanging water with the enclosing rock.

Obviously, if the initial concentration of water in the magma intruding into the stratum of enclosing rock at the given values of  $P_h$  and  $P_{H_20}$  is greater than the limiting concentration of water determined by the equilibrium of Model II, then the magma, tending toward equilibrium with the external medium, must give off water, i.e., a diffusion flow of water from the magma into the enclosing rock must form. Conversely, if the initial concentration of water in the magma is less than the limiting concentration of water at the given values of  $P_h$  and  $P_{H_20}$ , then the magma will absorb water from the enclosing rock, i.e., a diffusion flow of water from the enclosing rock into the magma will be observed.

For example, a magnatic melt with an initial water concentration corresponding to point A or C in Fig.4, intrudes into a stratum of enclosing rock and persists a considerable time under the conditions  $P_{H_{20}}$  = 500 atm,  $P_h$  = = 1000 atm. Since, to these conditions there corresponds the equilibrium concentration of water in the melt as represented by point B, it follows that the first magma ( $N_A > N_B$ ), as a result of mass transfer with the water of the enclosing rock, will give off water, while the second magma ( $N_C < N_B$ ) will on the contrary absorb it.

Thus, if for a saturated magma the release of water and its migration from the magmatic system into the enclosing rock is a necessary condition in any case for both Model I and Model II, then the necessary absorption of water of the enclosing rock by unsaturated magma can be true only for Model I. The unsaturated magma, according to Model II, can either absorb or give off water, and the direction of the diffusion flows of water in mass transfer must depend on the depths of deposition of the magma chamber, the vapor pressure of water in the enclosing rock, and the initial concentration of water in the magma coming from the depths to this level in the earth.

## 2. <u>Influence of the Radial Distribution of Water over the</u> Mass of the Melt, on Mass Transfer

The diffusion flows of water due to mass transfer with the surrounding medium must be in certain relations with those flows of matter which are bound to exist inside the magmatic melt if both temperature and gravitational fields exist in the system.

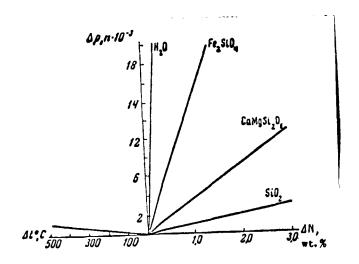


Fig. 5 Variation in Density of an Albitic Melt with Variation in Temperature and Concentration of the Components SiO<sub>2</sub>,

CaMgSi<sub>2</sub>O<sub>6</sub>, Fe<sub>2</sub>SiO<sub>4</sub>, H<sub>2</sub>O

The temperature of the melts in the system with the components SiO<sub>2</sub>, CaMgSi<sub>2</sub>O<sub>6</sub>, Fe<sub>2</sub>SiO<sub>4</sub> is 1400°C. The data on the water - albite melt relate to a temperature of 1200°C and a pressure of 2000 atm

This internal redistribution of matter in magmatic melts can be accomplished in two ways: by diffusion of particles of the melt, or as a result of the natural convective motion of the fluid.

The rate of convection, i.e., the macroscopic transport of matter, ordinarily is very much higher than the rate of diffusion (Bibl.12). Consequently, it may be assumed that, in the presence of natural convection in the magmatic fluid, this form of mass transfer will be predominant.

The natural convective motion in the molten mass within the gravitational field takes place spontaneously under the influence of forces exerted by the /513 density variation over the height of the liquid column when the density increases in directions radial to the earth's surface.

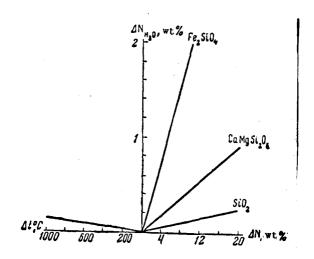


Fig.6 Relation between ΔN for Water, Silicate Components and Δt, Causing Equivalent Changes in the Density of an Albitic Melt (Plotted from the Data of Fig.5)

The appearance of a density gradient in this direction in the magma may be the result of a temperature drop of the melt toward the earth's surface, or a decrease in the concentration of the components. Figure 5 is a plot of the density variation of an albitic melt as a function of the concentrations of

silica, diopside, fayalite, and water, and under the influence of a temperature gradient. These values are calculated on the basis of the data given elsewhere (Bibl.13 - 16).

The calculations indicate that the density variation of the melt under the influence of the temperature gradient is incomparably less than the density variations that may be caused by even a small decline in the concentration of the silicate components and water. The greatest changes in the density of the melt are connected with the dissolution of water in it.

In Fig.6, the values of the  $\Delta N$  of the silicate component and the  $\Delta t$  that cause equivalent changes in the density of the albite melt are plotted against  $\Delta N$  for water. For example, a difference of 1 wt.% in the concentration of water between the upper and lower parts of a melt of specified height causes the same change in its density that could be caused under similar conditions by a difference of 70 wt.% in the concentration of silica (such a concentration lies outside the graph of Fig.6), of 21.5 wt.% of diopside, and of 5 wt.% of fayalite, while the changes of density under the influence of the temperature drop can  $\frac{5114}{2}$  be balanced by a literally infinitesimal  $\Delta N$  of the water.

As we see, the distribution of water through the mass of magmatic melt must play an exceptional role in the genesis of natural convection in that melt. Extensive changes in the concentration of the silicate components and the temperature throughout the mass of the melt are needed to counteract the movement of the magma portions with greater water content, i.e., with lower density, toward the roof of the magma chamber.

The direction of the diffusion flow of the water under the influence of gravitation can be defined by assuming, as before, an equilibrium distribution of water through the mass of the melt, beyond the limit which the magmatic sys-

tem should approach.

The influence of the gravitational field on the equilibrium in a water - albite melt had been calculated by Verhoogen (Bibl.7). These calculations were repeated by us on the basis of new experimental data in the albite - water system (Bibl.11), using an equation of the form

$$\left(\frac{dN_{\rm H,O}}{dh}\right)_T = \frac{N_{\rm H,O} (\overline{V}_{\rm H,O} \cdot \rho - M_{\rm H,O})g}{RT},$$

where  $M_{H_20}$  is the molecular weight of the water and  $\rho$  is the density of the water - albite melt. The results are shown in Fig.7. It will be seen that the

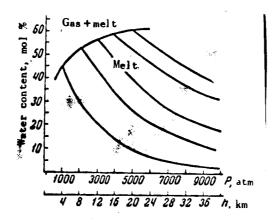


Fig.7 Gravitational Equilibrium of Water Distribution with Height of the Water - Albite Melt
The heavy curve indicates the conditions of the saturated state of the water - albite melt. Temperature 1200°C

equilibrium gravitational distribution of water must be characterized by an  $\rm H_2O$  enrichment of the upper part of the melt and by a considerable decrease in water content with depth.

At present, it is quite difficult to evaluate the influence of the temperature drop on the direction of the diffusion flow of water. In Kennedy's opinion (Bibl.17), the increase in the solubility of water in silicate melts seems to

indicate an increase in its concentration toward the colder margins of the magma, i.e., toward the roof of the chamber; however, from the thermodynamic point of view exactly the opposite variant is also possible. In any case, to judge by the equation, the temperature drop toward the upper parts of the melt should intensify the gravitational distribution of water, since this should increase with decreasing temperature.

In general there are reasons to assume that the redistribution of water through the mass of a magmatic melt is most probably accompanied by natural convection and by radial diffusion flow of water, leading to an enrichment of the upper parts of the magmatic melt in water.

A number of well-known geological facts, such as the location of the most intense transformations under the influence of the volatile components at the roof of magma chambers, might be considered a confirmation of this postulate.

Such distribution of water with height of the magma chamber should result /515 in a change in the conditions of mass transfer between the magma and the water of the enclosing rocks, with the depth of the magma chamber. The tendency of the magma to accumulate water in the upper parts of the chamber, and also a possible decrease in the vapor pressure of the water in the enclosing rocks toward the earth's surface, seem to speak in favor of an absorption of water in the lower zones of the magma and its extrusion in the upper zones.

If such a variant is possible, then the magmatic melt of greater radial extent would serve as a kind of conduit, through which the water absorbed from the enclosing rock at great depths is displaced by diffusion and convection toward the upper parts of the melt and there, in the form of a slow diffusion current, will again pass into the surrounding rock. It should be noted that the accumulation of water in the upper portions of the magma chamber may lead to a

supersaturation of the magma, which then would give off water in the form of an independent vapor phase where the separation of the water will have an effervescent character.

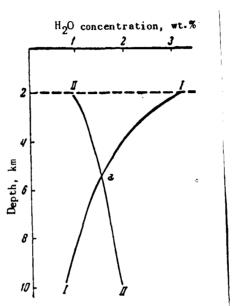


Fig.8 Equilibrium Distribution of Water through the Mass of Magmatic Melt (from the Example of a Water - Albite Melt) under the Influence of the Gravitational Field (Curve I-I) and in Mass Transfer with the Surroundings (Curve II-II) under Conditions when the Upper Parts of the Melt Are at a Depth of 2 km

Temperature of melt, 1200°C; pressure gradient of water in the surroundings, 100 atm/km; pressure gradient in the melt, 250 atm/km; the point a defines the depth at which inversion should take place under conditions of mass transfer with the extraneous water.

The water released in this manner will be a mixture of two types, primary magmatic water and water of the lower strata of the surrounding rocks.

From the available data, it is difficult to make a concrete evaluation of the depths at which inversion of the conditions of absorption and discharge of water should take place, under the influence of the internal redistribution of magmatic matter. This is primarily due to the absence of information on the pressure of water in the enclosing rock. In this connection, any calculations

of the point of inversion obviously are unreliable but may nevertheless be help-ful if they permit estimating the order of magnitude of the radial extension of magnatic bodies required for such an inversion.

Let us assume, in first approximation, that the pressure of water in the enclosing rocks is approximately equal to its hydrostatic pressure, i.e., that it amounts to about 100 atm/km. Under such conditions, the equilibrium distribution of water in the magmatic fluid is characterized by the curve II-II (Fig.8). It is to this distribution of water that the magma must tend, in its mass transfer with the environment. Curve I-I is the equilibrium gravitational distribution of water toward which the magma should tend as a result of the redistribution of matter under the action of the gravitational field.

Quite obviously, these tendencies are opposite; this should ensure the convection-diffusion transport of water of the magmatic fluid, as discussed above.

Under selected conditions for a magma chamber with its upper parts at /516 a depth of about 2 km, the point of inversion lies at a depth of  $\sim$  6 km (intersections of the curves I-I and II-II in Fig.8).

If the pressure of water in the enclosing rock is less than assumed in these calculations (100 atm/km), then the curve II-II (Fig.8) will shift toward lower water concentrations, and the point of inversion will be located at greater depths. Presumably, the pressure of water at great depth will be even higher (Bibl.1 - 3). This should shift the curve I-II toward higher water concentrations and the point of inversion toward more shallow depths.

It may be assumed on this basis that the radial extent of a magmatic melt of the order of 10 km is entirely sufficient for mass transfer with an inversion at great depth.

## 3. Possible Petrological Consequences of the Variation in Mass Transfer with Depth

Our analysis has been limited to the consideration of only a single component of the system, namely, to water. However, it is well known that ions and molecules cannot diffuse independently of each other, and that any diffusion is necessarily accompanied by a mass flow of matter, the so-called Stefanov flow (Bibl.18). The same is true of water. Its diffusion flow must necessarily be accompanied by a redistribution of other elements of the magmatic system.

In this connection, the variant of mass transfer in which the magma becomes a conduit for the dissolved water is of great geochemical interest. Here, the liquid magmatic mass, by convection and diffusion, may be an active carrier of matter extracted from the water at great depth. Thus, due to the principle of selective solution, the magmatic melt should become a kind of filter, collecting definite elements. In this differentiation of the solute, two main stages must be distinguished.

The first of these has to do with the distribution of matter between the water vapor and the enclosing rocks, and between the water vapor and the magmatic melt on dissolution of H<sub>2</sub>O in the magma; the second stage refers to the distribution of the magma components between the melt and the water, on ejection of the latter into the upper parts of the magma chamber in the form of a diffusion flow or in the form of water bubbles when the magma reaches the saturated state. Obviously, in both cases the water will extract and concentrate the readily soluble compounds, many of which, judging from contemporary experimental data, are connected with ore elements. On the ejection of water, both primary elements of the magma and elements, dissolved at great depth, will be entrained into the enclosing rocks.

This mass transfer, on extrusion of highly volatile components into certain parts of the magma chamber, may take place continuously for the entire period of time during which the magmatic fluid exists. Ultimately, and if the process continues for a long time, despite the insignificant contents of water and other elements in the magma the quantity of matter transferred together with the water may be very large. This should greatly increase the ore-forming potential of the magma.

### 4. Other Factors of Possible Influence on the Mass Transfer with Extraneous Water

In addition to the above causes, the extensive inhomogeneity of the rock, with respect to filtration, diffusive permeability, and water content, may also play a substantial role in mass transfer. This should lead to a considerable diversity in the conditions of mass transfer over the lithologic profile of the intrusive rocks.

It may be expected that in certain rocks, under the influence of the /517 magmatic heat, regions with higher pressure than in other types of rocks may be formed. In consequence of this, the magmatic melt may absorb water from some strata and discharge it into others.

#### CONCLUSIONS

The tendency of water - silicate melt systems toward conditions of equilibrium of the Model II indicates the following consequences of this process, to be expected in magmas in the presence of mass transfer with the water of the enclosing rock.

1. From the thermodynamic point of view, in the presence of mass transfer from and to the surrounding medium, magmatic melts saturated with water are an

unstable system and should give off water.

- 2. In unsaturated magmas the tendency toward equilibrium with the water of the enclosing rocks should lead to the appearance of diffusion flows of water. Their direction, whether from the magma into the enclosing rocks or from the enclosing rocks into the magma, depends on the depth of the magma chamber, the concentration of water in the magma, and on the vapor pressure of water in the enclosing rock.
- 3. The distribution of water through the mass of the magmatic melt, under the influence of the temperature and gravitational fields, permits the assumption of a variation in the conditions of mass transfer with the height of the magma column. The most probable version here is that the magma in its lower parts absorbs water and in its upper parts gives off water. This process should be favored by convection in the melt and by a radial diffusion flow of dissolved water toward the earth's surface.

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